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Electrogenerative formation of ferric ions in a sulfur dioxide–sulfuric acid solution; Graphite catalysed sulfur dioxide oxidation

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The electrogenerative oxidation of ferrous ions in 3 M sulfuric acid, containing sulfur dioxide and subsequent sulfur dioxide oxidation, were studied in connection with potential regenerable sulfur dioxide remediation processes. The presence of sulfur dioxide in the feed stream did not affect cell performance. Oxidation of sulfur dioxide in the electrogenerative reactor took place when high ferrous to ferric ion conversions were obtained. Low cost graphite and iron ions served as an effective mediating system for promoting electron transfer to sulfur dioxide in strong acid solutions. In contrast, the homogenous reaction between iron(III) and sulfur dioxide is relatively slow. In a separate batch reactor, the heterogeneous iron(III) and sulfur dioxide reaction was found to be graphite catalysed, accounting for sulfur dioxide conversion observed in the electrogenerative reactor. Ferrous ion presence should be minimized, because it inhibits the desired catalysed reaction.

Keywords: *ferrous inhibition*, *mediated oxidation*, *remediation*

1. Introduction

Sulfur dioxide control remains a pressing concern with annual global emissions estimated at near 75 million tonnes from combustion and industrial sources [1, 2]. Regenerable processes for desulfurization allow reuse of the sorbent and produce potentially useful sulfur compounds, and thus, are of increasing interest [3]. Many strategies for removing sulfur dioxide involve oxidation and a number of electrochemical processes have been proposed, but most require power input to drive the reaction [4–7]. The electrogenerative approach, however, generates d.c. current with positive potential. Favourable thermodynamics provide the electrochemical driving force for desired reactions without an external power source [8, 9]. Many of the processes involve the overall reaction of sulfur dioxide with oxygen to produce sulfuric acid. Electrochemically, the direct reactions may be represented as follows:

anode:

$$2SO_2.H_2O + 2H_2O \rightarrow 2H_2SO_4 + 4H^+ + 4e^- \quad E = 0.17\,V\,vs\,SHE \qquad (1)$$

cathode:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad E = 1.229\,V\,vs\,SHE \qquad (2)$$

overall:

$$2SO_2.H_2O + O_2 \rightarrow 2H_2SO_4 \quad E = 1.06\,V\,vs\,SHE \qquad (3)$$

Neither electrode operates reversibly, but power is readily generated from the couple. Efficient electrocatalysts are used to achieve a significant reaction rate. Often noble metals, dispersed on conductive supports, have been employed, and current densities of $0.6\,A\,cm^{-2}$ are obtainable in driven systems [10–12]. However, economic considerations favour development of alternative catalytic systems. Carbons and graphites are chemically inert as electrodes and are attractive from a cost viewpoint, but alone exhibit limited kinetic activity for sulfur dioxide oxidation [12–14]. Rate enhancement may be obtained by employing a mediator to provide an alternate reaction route between the electrode and reacting species. Conceptually, an active intermediate is electrochemically generated and then chemically reacted with the species of interest to reproduce the starting reagent. Ideally, both reaction steps occur sequentially in the same reactor, provided the other reactant does not interfere. Of the various transition metals or halide ions, employed as electron transfer agents, the low cost and high reactivity of the iron redox couple make it particularly attractive. This investigation of graphite with mediating iron ions in the presence of sulfur dioxide is part of a broad search for viable alternatives for sulfur dioxide oxidation in sulfuric acid solutions. It examines the effect of combining iron ions and sulfur dioxide in a hybrid continuous flow electrogenerative reactor. Both were studied separately, earlier [8, 9]. Reactions with two oxidiz-

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able species may occur simultaneously or in series as in a mediated process.

Mediators have often been considered in removing sulfur dioxide from aqueous solutions, because of environmental concerns. The reaction of iron and sulfur dioxide is particularly well studied [5, 6, 8, 15–19], mainly in dilute solutions at near neutral pH. Regeneration of the mediator to the oxidized form can be accomplished by passage through an electrochemical cell or by direct reaction with molecular oxygen. For iron ions in sulfuric acid, involving mediation, the overall reactions might be represented as follows [9].

$$4\ Fe^{2+} + 4\ H^+ + O_2 \rightarrow 4\ Fe^{3+} + 2\ H_2\ O \qquad E^\circ_{cell} = 0.55\ V \qquad (4)$$

$$2\ Fe^{3+} +\ SO_2 + 2H_2O \rightarrow 2\ Fe^{2+} +\ H_2SO_4 + 2H^+ \qquad \Delta G = -115.8\ kJ \qquad (5)$$

The iron(III) sulfur dioxide mediated process is slow in strong acid. Reactions in aqueous solution proceed through a series of iron–sulfur complexes, involving two one-electron transfers [15–19]. The acidity of the reacting solution determines the concentration and reactivity of initial species with the most kinetically inert forms of sulfur and iron species found at high acid conditions. Considering S(IV) compounds, for example, reaction with ferric ions is significantly faster with bisulfite (HSO_3^-) than with dissolved sulfur dioxide ($SO_2.H_2O$), which is the predominant species at a pH below 2 ($pK_{a1} = 1.86$, $pK_{a2} = 7.2$) [5, 15–20]. With increased acidity, which may be a consequence of continued reaction, the homogenous reaction rate decreases with conversion so that the reaction rate becomes impractically small at ambient conditions if no provisions are made to keep the pH relatively high [18]. Kinetics for the ferrous to ferric regeneration reaction with molecular oxygen are also constrained in the low pH region [6]. This reaction may be promoted by higher temperatures and oxygen pressures [21] or alternatively by electrochemical oxidation with a graphite anode [6, 9]. Application of more severe conditions and/or dilute solutions with higher pH to enhance the reactions can run counter to requirements for commercial recovery of sulfuric acid, where higher sulfuric acid concentrations would be of interest. Thus, it would be advantageous to have access to a process for oxidizing sulfur dioxide in strong acid solutions. Ce(III)–Ce(IV) and Ni(III) (cyclam), which have significantly higher oxidation potentials than iron, have been proposed for operation in strong acid solutions [22, 23], but both require an external power source.

Electrochemical reactions as component parts of overall transformations can proceed in strong acid solutions. In previous work, it was shown that dissolved sulfur dioxide can be electrogeneratively oxidized in direct fashion with platinum/graphite packed-bed electrodes or indirectly with an iodide/iodine redox couple on graphite electrodes with current densities as high as 100 mA cm^{-2} for either system in 3 M sulfuric acid [8]. Unfortunately, both utilize expensive catalysts.

As a cost effective alternative and prelude to this and other work, the electrogenerative oxidation of ferrous ions in sulfuric acid with graphite electrodes was investigated [9]. Using packed-bed graphite electrodes, equally high current densities of 100 mA cm^{-2} were obtained from ferrous-sulfuric acid solutions with an oxygen cathode. It is thus possible to envision a process whereby the catalytic efficiency of the graphite ferrous reaction is exploited with the product serving to oxidize sulfur dioxide, without the need for employing expensive catalytic agents for the anode. The utility of the graphite-iron system is somewhat offset by the slow reaction kinetics of ferric ion with sulfur dioxide in strong acid solutions [6]. Although neutralization or dilution may enhance the reaction rate, it would seem desirable to obtain potentially useful sulfuric acid from sulfur dioxide oxidation. We have found through the present work that another method is viable. A graphite surface can catalyse the iron(III)–SO_2 reaction heterogeneously, making it possible to conduct at least part of the mediated process *in situ*, that is, within the confines of the electrochemical reactor. Possibilities for graphite catalysis are of interest, because the slow rate of the uncatalysed Fe(III)–SO_2 reaction at lower pH has limited further development of the ferric ion system. Means for decreasing costs at the cathode are not discussed here. However, loadings of expensive catalysts on gas diffusion electrodes are continually being lowered through research.

The present experiments were directed toward exploring the feasibility of a mediated graphite iron system in the presence of sulfur dioxide and to identify conditions required to convert SO_2 under high acid concentration (3 M sulfuric acid). Since performance in electrogenerative cells is a reflection of the electrochemistry, current-voltage plots and product analysis can be used to give insights into the reaction processes. Performance curves from the electrogenerative cell were collected under a complete range of iron(II), iron(III) and sulfur dioxide concentrations at varying flow rates. The electrogenerative reactor, operating with a mixed iron–sulfur dioxide feed, responded strongly to iron, but was weakly influenced by the presence of sulfur dioxide only under conditions near limiting current where in-cell conversion of SO_2 was found to be maximized. The requirement of a high iron(III) to iron(II) ratio for in-cell SO_2 conversion can be explained using the results of a separate graphite batch reactor study. The graphite catalyses the iron(III)–SO_2 reaction, but the reaction is somewhat inhibited by the ferrous ion product.

Earlier work suggested that cupric ion may help catalyse the mediation reactions between iron ion and sulfur dioxide [5, 9, 21]. Thus, in several of the electrochemical experiments here, copper(II) was investigated as a cocatalyst, but the cupric ion significance in aiding electron transfer was not established.

2. Experimental details

2.1. *Electrogenerative reactor and operation*

The hybrid electrogenerative cell, schematically represented in Fig. 1, consisted of a rectangular graphite packed-bed anode separated from an oxygen gas diffusion cathode by an anion exchange membrane. Experimental details concerning operation of the cell and equipment have been previously described [8, 9, 24]. The graphite (Desulco, US Mesh 16–18, Superior Graphite Company), used in the packed-bed anode, was precleaned by soaking in concentrated sulfuric acid for one hour, followed by rinsing with deionized water before the first use. The same graphite sample (2.6 cm^3) was used throughout the investigation. After each use it was washed with deionized water and stored in 0.5 M sulfuric acid. The sample was packed into the anode chamber of approximately equal volume (51 mm × 12.7 mm × 4 mm) and a platinum current collector (45 mesh) was positioned on the front face of the packed-bed to provide compression and electrical contact (packed-bed void volume 1.4 cm^3). In all experiments the cathode was an American Cyanamid LAA-2 gas diffusion electrode (9 mg of Pt cm^{-2} with Teflon on a tantalum screen) which provided high performance and excellent reproducibility [8]. As with the anode, electrical connection to the cathode was made via a platinum current collector. The anode and cathode compartments were separated by a RAI Research Corp. anion exchange membrane (R-4030) to limit deactivation of the oxygen cathode by migrating iron ions and to experimentally isolate the electrodes. Changing conditions in the anode compartment were not reflected in the cathode response. During reactor operation, the anode potential was monitored relative to a NaCl saturated calomel reference electrode (SSCE), connected to the back side of the packed bed by a Luggin type connector. This arrangement was occasionally altered and the cathode potential was measured through the catholyte feed line [25].

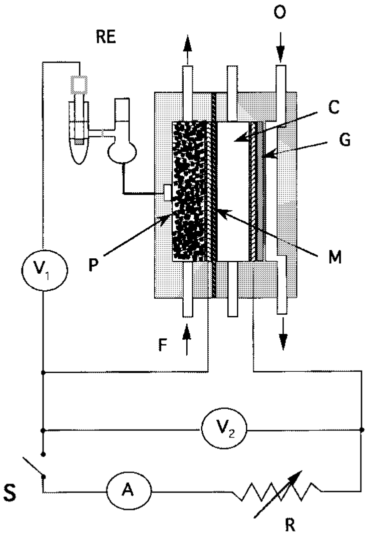

Fig. 1. Schematic of the electrogenerative cell and electronic circuitry. (A) ammeter, (C) cathode electrolyte compartment, (F) anolyte feed, (G) gas-diffusion oxygen electrode, (M) anion-exchange membrane, (O) oxygen gas inlet, (P) graphite packed-bed electrode, (R) variable resistor, (RE) reference electrode, (S) switch, (V$_1$, V$_2$) high impedance voltmeters.

Before operating the cell, the electrodes were conditioned to ensure reproducible electrocatalytic activity. With 3 M sulfuric acid present in both cell compartments, any platinum oxides on the gas cathode were reduced with a flow of hydrogen gas. After 10 min electrical connection to the anode was made and the cell was quickly brought to a short circuit condition, generating a maximum current of 5 mA that rapidly decreased. If the cell voltage failed to decrease to near 0 V within 10 min, a reducing current of 1 mA or less was applied to the anode with an external power supply to reach a cell potential near 0 to 0.5 mV.

After disconnecting the power supply the SSCE potential was referred to the hydrogen electrode (RHE). The flowing hydrogen gas (over the gas diffusion electrode) was replaced by nitrogen and then oxygen. Current (5 mA) was allowed to flow until the anode potential rose above 250 mV to oxidize residual hydrogen in the anode compartment. The internal resistance of the cell was determined in several of the polarization experiments with an interrupter switch (The Electrosynthesis Company, model 800), which measured the resistance voltage drop of the operating cell. Since the cell configuration and solutions were not altered, the same resistance values were assumed for those experiments in which no measurements were made. Cell resistance values obtained using a milliohmmeter were found to be unreliable with a graphite electrode.

For polarization experiments, the anolyte sulfuric acid solutions, containing the iron and sulfur dioxide (and occasionally copper), were permitted to flow into the anode compartment at a feed rate between 0.3 to 5 ml min^{-1}. Polarization curves of the electrochemical reactor were obtained by varying the external load resistor from open circuit. A 3 min time interval was adequate for achieving a steady state current and voltage at each new resistance setting. All experiments were conducted at ambient temperatures, around 23 °C. The sulfuric acid catholyte was renewed with a flow system in the time period between successive polarization experiments, but was generally kept immobile during data collection. In the analysis of the reactor effluent, the electrogenerative cell was operated at steady state for 10 min before sample collection.

2.2. *Solution preparation*

The anolyte solutions were considered to be somewhat sensitive to atmospheric oxidation of the iron(II). Therefore, solutions were prepared and used with efforts to avoid exposure to oxygen. Appropriate amounts of iron(II) sulfate salts were added to inert gas purged sulfuric acid and were mixed in closed flasks. After the dissolution of the metal salts the desired concentrations of sulfur dioxide were usually obtained by adding a SO_2 saturated sulfuric acid solution (prepared by bubbling SO_2 at 1 atm through the acid) to the iron solution. Measurements indicated that under the ambient conditions and methods employed in this study maximum concentrations of SO_2 in 3 M sulfuric acid ranged from 0.6 to 1.2 M. Higher sulfur dioxide concentrations were difficult to maintain, given that the solutions rapidly lose SO_2 and as a consequence were seldom used (Henry's law constant 0.71 atm M^{-1} for 3 M sulfuric acid at 20 °C). A typical 3 M sulfuric acid anolyte consisted of a 15% saturated solution of SO_2 (often about 0.11 M) with 0.2 or 0.4 M ferrous sulfate. The actual SO_2 concentration was determined by chemical analysis. Since the electrochemical reactor response was affected by the presence of ferric ion [9], which forms upon exposure to the atmosphere, the ferrous containing anolyte solutions were protected from oxidation by a stream of nitrogen gas flowing over the top of the reaction flask. This led to loss of sulfur dioxide from solution by removal with the gas stream. However, this loss was not experimentally significant, since it was found that the SO_2 concentration in this range had a negligible effect upon the reactor performance under our conditions (*vide infra*). Most values given for the SO_2 concentration here represent the initial concentrations before the polarization experiment, and are indicated as such. The SO_2 concentration after the polarization runs was roughly half the initial value. In a few experiments the anolyte solutions were prepared using an alternate method to establish a more constant SO_2 concentration without introduction of oxygen. A nitrogen–SO_2 gas mixture ($\sim 30\,cm^3\,min^{-1}\,N_2$ and $4–30\,cm^3\,min^{-1}\,SO_2$) was bubbled continuously through the ferrous sulfuric acid solution. Several hours were allowed for equilibration before the anolyte was used. The sulfur dioxide concentration was again determined by analysis.

2.3. *Sampling and chemical analysis*

The anolyte and the electrogenerative cell effluents were individually analyzed for each of the reactants and products, using known titrimetric or spectrophotometric techniques, and modified as required for the more complex matrix. Sulfur dioxide was analysed via an iodiometric method by reacting a molar excess of the triiodide solution with the sample, followed by back titration with sodium thiosulfate [24, 26]. Since ferric ion also reacts with triiodide ion, the reactor effluent from an operating cell could not be directly measured [27]. The SO_2 separation was accomplished by passing a stream of nitrogen through the collected effluent, followed by trapping all entrained sulfur dioxide in a 0.1 M NaOH solution [28]. This solution was acidified and treated as above with the triiodide solution. In each step of the analysis the SO_2 must be efficiently captured or transferred. To reduce SO_2 loss during cell effluent collection, a tight fitting collection flask with a Teflon gasket was placed at the reactor outlet. Simultaneously, the collection flask was also cooled in ice to reduce SO_2 volatility. During the subsequent purging stage with nitrogen, the collection flask was occasionally warmed to increase the SO_2 removal rate. The anolyte, now free of SO_2, was subsequently used in the other analyses for both iron ions and sulfuric acid. The hour long nitrogen purge caused a slight evaporative water loss, requiring correction.

For determination of sulfuric acid by base titration, it was necessary to add a chelating agent to complex the iron and copper ions in order to avoid metal hydroxide formation [21]. Samples containing a molar excess of EDTA to iron (ratio 1.3 to 1) were titrated with 0.1 M NaOH using magnetic stirring to a pH of 8.2, determined with a pH meter.

The iron species in the purged effluent were spectrophotometrically determined. A standard method, involving 1, 10-phenanthroline, was used for ferrous ion determination with detection at 512 nm to prevent interference from the more weakly colored Fe(III) phenanthroline complex; except no reducing agent was used to convert the ferric ion [29].

In more concentrated sulfuric acid solutions iron(III) forms a strongly absorbing complex, useful for spectral analyses at wavelengths below 400 nm [30, 31]. Iron(III) samples were diluted using 3 M sulfuric acid to an appropriate concentration range between 0.5 and 3 mM and read at 350 nm with 3 M sulfuric acid as the reference. Under these conditions ferrous ion (and sulfur dioxide, when present) was weakly absorbent. Calibration standards replicated the sample solutions. The low concentration of copper ion present in some samples was not found to interfere with the iron analyses.

2.4. *Batch reactor graphite catalysis*

Experiments on graphite catalysed reactions of iron(III) with sulfur dioxide were conducted in 100 ml round bottom flasks with 2.2 g of 20–30 mesh Desulco graphite (BET surface area $0.95\,m^2\,g^{-1}$) at ambient temperatures (near 24 °C) using 80 ml of reacting solution (initially 0.040 M Fe(III), 0.11 M SO_2 in 3 M sulfuric acid). A sulfur dioxide–nitrogen gas stream ($22\,cm^3\,min^{-1}\,N_2$, $3.9\,cm^3\,min^{-1}\,SO_2$) was passed through the solution to maintain the SO_2 concentration and prevent side reaction with oxygen. A second flask also contained 0.049 M Fe(II) in addition to the Fe(III) and SO_2. Periodically, small aliquots (0.3 to 0.4 ml) were withdrawn for ferric ion analysis, using the spectrophotometric method, described above. The solutions were stirred continuously for about 8 h, and thereafter only intermittently to reduce formation of graphite fines. The homogenous reaction was simultaneously monitored by placing the reaction solution in closed vials, which were analyzed as required.

3. Results and discussion

An important goal was to study the electrogenerative oxidation of sulfur dioxide under strong acid conditions using the graphite iron mediating system. The presence of two oxidizable species (Fe(II) and SO_2) in the anolyte feed of the electrogenerative reactor presented a special challenge. Fuller understanding of the electrochemistry was achieved by operating the continuous-flow electrogenerative reactor at different flow rates with a variety of anolyte solution compositions, containing mixtures of Fe(II), SO_2, and Fe(III). Comparison of the polarization curves permitted inferences concerning the nature of the electrochemical reactions, these were supported by product analyses of the reactor effluent. Conversion of the sulfur dioxide in the electrogenerative reactor was promoted by cell operation near limiting current conditions where there is high ferric to ferrous ion ratios at the graphite surface. Explanation of the sulfur dioxide conversion and the iron ion ratio was obtained from a separate batch reactor study, in which graphite catalysis of the iron(III)–sulfur dioxide reaction also was established.

3.1. *Electrogenerative reactor*

Since in the sulfur dioxide conversion process under consideration the electrogenerative reactor feed would contain an aqueous mixture of iron ions with sulfur dioxide, the influence of the combined species on the electrochemistry should be considered. In one extreme scenario, the two oxidizable species might compete electrochemically (Reactions 1 and 4, in parallel). At the other extreme, one of the two species might completely dominate the electrochemical oxidation reaction. Under iron control (i.e., the only electrochemical reaction is ferrous to ferric ion), the mediation concept would be fulfilled. The possible electrochemical reactions depend not only on the reactivity but also on the adsorptivity of each species. Thus, the combined behavior of Fe(II) and SO_2 was a key consideration of the investigation. It was previously established that alone, the electrogenerative reaction of sulfur dioxide on graphite was slow, while the oxidation of ferrous ion was rapid [8, 9]. Without considering adsorption the iron reaction should dominate the electrochemistry. Sulfur dioxide oxidation might occur by mediated reaction with the ferric ion product.

The polarization data, as shown in Figs 2–4, clearly establish the iron reaction as predominant. Under most of the investigated conditions, only the iron concentrations and flow rates were important. Exceptions were under conditions of low flow rate or anolyte solutions with ferric ion. Figure 2 shows the cell voltage performance curves obtained from various sulfur dioxide, ferrous ion (0.2 M), and cupric ion solution combinations in 3 M sulfuric acid at flow rates near 1.2 ml min^{-1}. The data may be divided into two groups, based solely on iron. With only sulfur dioxide (0.15 M) in 3 M sulfuric acid, the cell strongly polarized, yielding a maximum current density of 6 mA cm^{-2} from direct oxidation with the packed bed graphite electrode. With 0.2 M iron(II) present, the polarization was significantly reduced and currents up to 40 mA cm^{-2} were achieved, independent of the presence of sulfur dioxide or cupric ion. Under these conditions the iron reaction is in control and there is no evidence of interference or a competing sulfur dioxide electrochemical reaction. This is further demonstrated in Figs 3 and 4 by individually varying the reagent concentrations to a greater extent. By doubling the iron(II) concentration from 0.2 to 0.4 M, as seen in Fig. 3, the current was greatly increased at a given anode potential. In contrast, large changes in the sulfur dioxide concentration from 0 to 0.42 M with constant 0.2 M Fe(II) (Fig. 4) had a negligible effect on the cell voltage curves. Even at a concentration

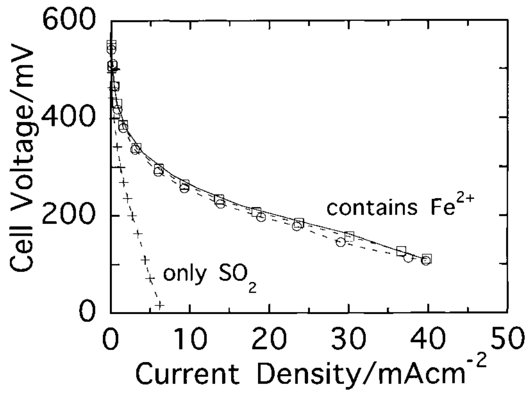

Fig. 2. Performance curves showing cell polarization of a graphite packed bed electrode from various sulfur dioxide, iron(II) and copper(II) solutions in 3 M sulfuric acid in conjunction with an oxygen gas diffusion electrode. (+) 0.19 M SO_2 (initial concentration) at 1.2 ml min^{-1}; (solid line) 0.2 M Fe^{2+} at 1.1 ml min^{-1}.; (□) 0.2 M Fe^{2+}, 0.2 M SO_2 (initial) at 1.2 ml min^{-1}; (○) 0.2 M Fe^{2+}, 0.02 M Cu^{2+}, 0.2 M SO_2 (initial) at 1.3 ml min^{-1}. Cell voltage curves corrected for internal resistance loss, $R_{int} = 0.33\,\Omega$

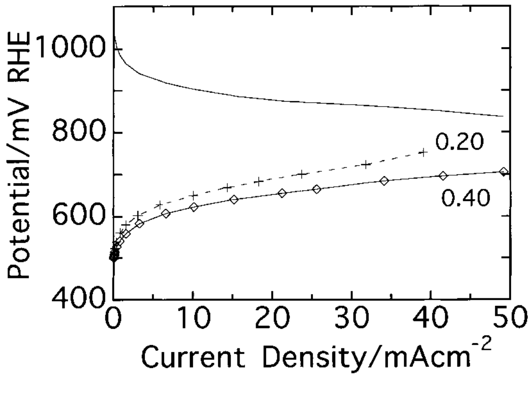

Fig. 3. Anode polarization curves from iron(II) and sulfur dioxide solutions, showing effect of changing ferrous ion concentration in the electrogenerative reactor. (+) 0.2 M Fe^{2+}, 0.13 M SO_2 (initial) at 1.2 ml min^{-1}; (◊) 0.4 M Fe^{2+}, 0.12 M SO_2 (initial) at 1.3 ml min^{-1}. Representative cathode polarization curve shown as a solid line. Cell voltage is difference between cathode and anode curves.

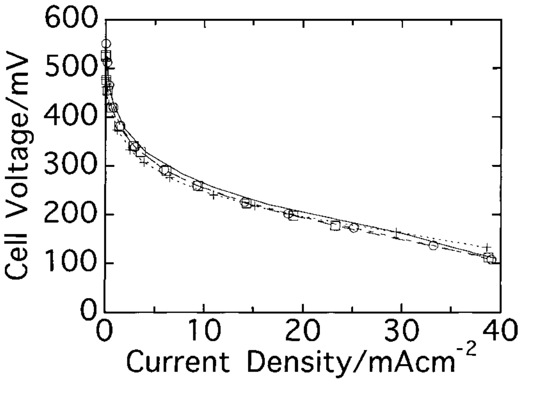

Fig. 4. Cell voltage polarization curves from a 0.2 M Fe^{2+} in a 3 M sulfuric acid solution containing varying concentrations of sulfur dioxide, corrected for ohmic loss, $R_{int} = 0.33\,\Omega$ from electrogenerative cell. (solid line) No SO_2 at 1.1 ml min^{-1}; (○) 0.13 M SO_2 at 1.3 ml min^{-1}; (+) 0.22 M SO_2 (fixed concentration) at 1.3 ml min^{-1}; (□) 0.42 M SO_2 (fixed concentration) at 1.5 ml min^{-1}.

(0.42 M) more than double the Fe(II) (0.2 M), sulfur dioxide still did not affect the polarization curve, and presumably does not compete with the iron electrochemical reaction on graphite. The absence of interference from incorporated sulfur dioxide in ferrous anolyte solution is important from the standpoint of an iron(II) regeneration process. Sulfur dioxide removal is not required for ferrous to ferric oxidation. At the maximum current density of 40 mA cm^{-2} with a flow rate of 1.2 ml min^{-1} the single pass conversion of 0.2 M ferrous ion is approximately 67%, when based coulometrically on the ferrous to ferric reaction. Cupric ion presence does not significantly improve performance under these conditions and appears to be innocuous.

Thus far, the data presented were collected at a relatively rapid flow rate of 1.2 ml min^{-1}. With anolyte flow reduced, the situation may be altered as the iron(II) is depleted in the anolyte by passage through the cell. Previous work on iron(II) oxidation with graphite electrodes showed a strong flow rate dependence on the cell polarization [9]. Figure 5 shows the anodic polarization curves of a 0.2 M Fe(II) solution, containing 0.1 M SO_2 and 0.02 M Cu(II), compared with a 0.2 M Fe(II) solution at two sets of flow rates centered around 0.36 and 0.7 ml min^{-1}. Maximum current densities were around 19 and 33 mA cm^{-2} for each respective flow. The polarization curves are essentially the same for solutions of Fe(II)-SO_2–Cu(II) and Fe(II) (alone) at the higher flow, but differ significantly at the lower flow, indicating that SO_2 is beginning to react. The increase in the slope of the polarization curve (starting at 10 and 20 mA cm^{-2}) at the slower flow rates imply the onset of concentration polarization. It is beneficial to ascertain the single pass conversion of ferrous ion to ferric ion, based on the current. For the ferrous solution (0.357 ml min^{-1}) the calculated conversion is 104% (a slightly unstable flow probably explains the somewhat high value over a 100%), showing that limiting current has been reached. The cell is operating under mass transfer control. For the ferrous sulfur dioxide mixture, the conversion is even higher 112% (0.375 ml min^{-1}), indicating that in addition to iron, SO_2 is contributing to the current and is being converted in the electrochemical reactor. At the slightly higher flow rates, conversion of iron is not complete (85% for the Fe(II) solution and 95% for the mixture). Apparently, before sulfur dioxide can be converted in the electrogenerative reactor, ferrous ion must first be oxidized, and this occurs to the greatest extent at slow flows.

The electrogenerative cell had been operated with only ferrous and sulfur dioxide anolyte mixture feed. The effect of ferric ion had not yet been determined. Given the results above, added ferric ion should more readily cause an observable polarization difference with the solution containing sulfur dioxide. Indeed this appears to be the case as shown in Fig. 6 for polarization curves from a ferrous-ferric mixture (each 0.1 M) at flow rates near 1.2 ml min^{-1}. The solution of mixed iron ions, containing additional 0.06 M SO_2, showed a substantial increase in current compared with the iron ion mixture without SO_2, unlike the ferrous solutions at 1.2 ml min^{-1} (Figs 2 or

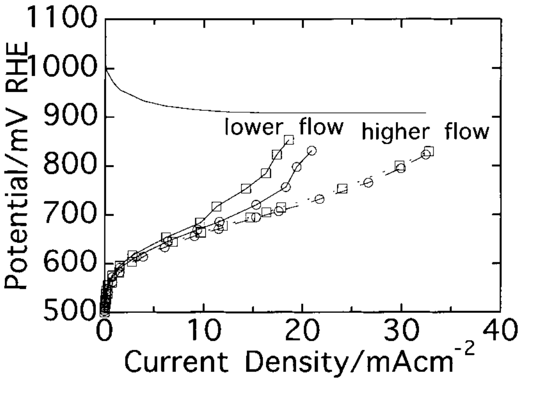

Fig. 5. Anodic polarization curves from Fe^{2+} and $Fe^{2+}/Cu^{2+}/SO_2$ solutions in 3 M acid at reduced flows. (□) 0.2 M Fe^{2+}, solid line at 0.36 ml min^{-1} and dashed line at 0.77 ml min^{-1} in electrogenerative reactor. (○) 0.2 M Fe^{2+}, 0.02 M Cu^{2+}, 0.07 M SO_2 (initial concentration) solid line at 0.38 ml min^{-1} and dashed line at 0.69 ml min^{-1}. Cathode polarization curve shown as a solid line without data points.

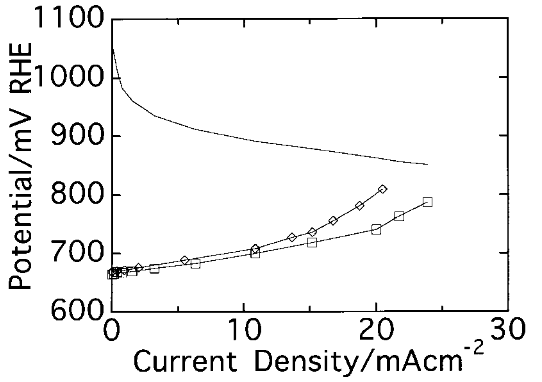

Fig. 6. Anode polarization curves from 0.1 M Fe^{2+} and 0.1 M Fe^{3+} solutions in electrogenerative reactor, showing effect of mixed iron solutions on SO_2 oxidation. (◊) no added SO_2 at 1.2 ml min^{-1}; (□) with additional 0.06 M SO_2 (initial) at 1.3 ml min^{-1}. Cathode polarization curve is shown as a solid line.

4), which yielded like polarization data. The extra current is attributed to sulfur dioxide conversion to give more ferrous ion. The shape of the polarization curve with the sharper rise in the slope is again suggestive of concentration polarization effects, which promote the onset of the sulfur dioxide reaction. The added ferric ion did not appear to interfere with the electrochemical oxidation (a current over 20 mA cm^{-2} was obtained from 0.1 M ferrous ion), and apparently promotes SO_2 reaction even at higher flow rates.

The polarization curves (Fig. 6), arising from the iron mixture, also differ from the previous curves for ferrous ion (Fig. 3) by having significantly higher open circuit voltages for the graphite anode (668 mV compared with 500 mV for the 0.2 M Fe(II) solutions); a result of the ferric ion. Previous work showed that the open circuit voltages for iron ion varied in a Nernstian manner [9], suggestive of reversible reaction kinetics, which is also reflected by the modest polarization increase, seen in Fig. 6.

Operation of the electrogenerative cell has not yet been described with the limiting solution combination of ferric ion and sulfur dioxide (no ferrous). Reactions are controlled by iron(II) presence, and only when iron(II) is depleted or restricted that observable effects first appear from sulfur dioxide. A ferric-sulfur dioxide solution will cause the sulfur dioxide oxidation reaction. Shown in Fig. 7 are the anodic polarization curves from such a solution mixture compared with a sulfur dioxide solution on the graphite electrode. Without sulfur dioxide a ferric solution yields no current and yet the polarization curve of the mixture resembles the previous iron data (Fig. 6) and not sulfur dioxide. The high value for the open circuit voltage (707 mV) and the uniform shallow polarization increase are good indicators of an iron influenced electrochemistry. With this solution mixture, sulfur dioxide must first react with ferric ion in the electrogenerative cell, followed by rapid electrochemical oxidation of the ferrous ion. Chemical analysis of the cell effluent showed that all iron remained in the higher oxidation state; consequently, the observed current can be directly ascribed to mediated SO_2 oxidation.

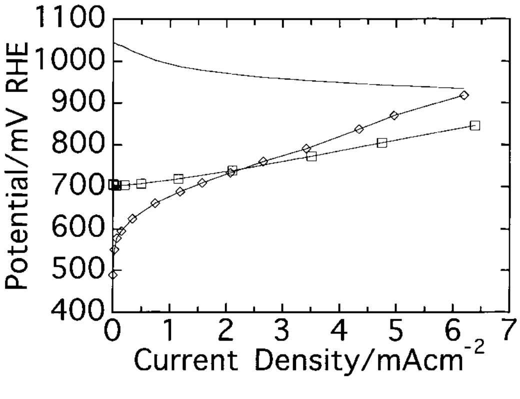

Fig. 7. Anode polarization curves from sulfur dioxide solutions with added ferric ion. (□) 0.17 M SO_2 (fixed concentration) with 0.09 M Fe^{3+} at 0.84 ml min^{-1}; (◊) 0.19 M SO_2, initial concentration at 1.2 ml min^{-1}. Cathode polarization curve is shown as a solid line without data points.

3.2. *Chemical analysis*

Polarization data collected from the electrogenerative cell implied that SO_2 did not significantly participate in reactions in the electrochemical reactor unless the cell was operated at high conversions of the more reactive ferrous ion, or ferric ion was initially present with ferrous in the anolyte. Because multiple reaction pathways both electrochemical and chemical are possible, quantification of the sulfur dioxide conversion requires additional chemical analysis of the reactor effluent. Chemical reaction of ferric ion with sulfur dioxide can occur after the electrochemical step and may not be reflected in the electrochemical response.

For determining the effectiveness of the reactor for converting sulfur dioxide, two approaches were taken. The conversion can be directly determined by measuring the decrease in the sulfur dioxide concentration of the anolyte after passage through the cell. Likewise, the increased sulfuric acid concentration may serve as an independent check. The conversion of sulfur dioxide may also be obtained in an indirect manner by determining changes in the iron concentrations and relating the measured value to calculated changes, derived from current and flow data, assuming only an iron reaction. Differences between the actual and calculated values are attributed to the sulfur dioxide reaction.

Two ferrous sulfur dioxide solutions (one contained 0.02 M cupric ion) were run through the cell at varying flow rates near maximum current conditions. Table 1 shows the analyses results from four experiments. The first two columns indicate the experimental details, the third the calculated iron conversion, while the last five present the analyses data for the iron and sulfur species. The final three columns represent the sulfur dioxide conversion (in terms of the molar change) and are roughly equivalent for each of the four experiments.

As a whole, the data are consistent, both in terms of the mass balances of the iron or sulfur species, but also more broadly with conclusions drawn from the polarization experiments. The molar balances of the ferrous–ferric data are in accord to within 4%, while the sulfur compounds vary up to near 50% for an individual experiment, reflecting greater errors associated with the SO_2 and sulfuric acid analyses. Hence, of the last three columns in Table 1, which show sulfur dioxide conversion, the final one is more reliable, since it is based on the iron data.

The polarization experiments indicated that flow rate was an important factor in determining sulfur dioxide reactivity. Chemical analyses quantify the effect. At 1.2 ml min^{-1} (experiment A in Table 1) the amount of SO_2 reacted is small (conversion is at most under 8%), in spite of an iron conversion that exceeds 67%. With lower flow rates (experiments A to C),

Table 1. Analysis results of electrogenerative reactor effluent under varying flow for assessment of sulfur dioxide conversion

Experiment–solution	*Flow Rate* /ml min^{-1}	*Iron analyses*			*Sulfur dioxide conversion* (M)		
		Calculated [*Fe*] *converted*‡/M	Δ[*Fe*(*II*)] /M	Δ[*Fe*(*III*)] /M	$\Delta[SO_2]$ /M	ΔH_2SO_4 /M	*Calculated* $\Delta[SO_2]$/M§
A* Fe/Cu	1.21	0.150	0.133	0.133	0	0.006	0.0085
B* Fe/Cu	0.597	0.199	0.169	0.175	0.014	0.024	0.015
C* Fe/Cu	0.276	0.267	0.185	0.187	0.025	0.038	0.040
D† Fe	0.271	0.273	0.199	0.206	0.030	0.017	0.030

* Initial composition 0.196 M Fe(II), 0.006 M Fe(III), 0.0207 M Cu(II) 0.11 M SO_2, 2.986 M H_2SO_4.

† Initial composition 0.213 M Fe(II), 0.065 M SO_2, 2.991 M H_2SO_4.

‡ Theoretical iron converted based on current and flow rate, assuming that iron is the only reactive species.

§ Derived from the difference between the theoretical iron converted and actual conversion based on Fe(II) data.

SO_2 conversion increases to 36%. Even at moderate flow (experiment B), where 86% of the Fe(II) was transformed, the conversion of SO_2 was a modest 14%. The final two experiments (C and D) differ in terms of the SO_2 concentration and the presence of copper ion; nonetheless, the amount of SO_2 reacted in D is still significant, although less than in experiment C (conversion in D is higher 46%), showing that iron alone can function as the mediator, and copper is not essential under these conditions. Any positive catalytic effect associated with the cupric ion is small under these test conditions.

A meaningful conversion of sulfur dioxide can occur within the electrogenerative cell using a 3 M sulfuric acid ferrous solution. However, as evidenced by the polarization data, iron conversions to the trivalent state must be relatively large and approach 94% at the slowest flow. Consequently, the generated ferric ion could be used for removing the unreacted SO_2 in a second graphite catalysed chemical reactor. The possibility of chemical conversion in this reactor is demonstrated in the next section.

3.3. *Graphite catalysis*

In the sulfur dioxide removal process under consideration, generated ferric ion must react with sulfur dioxide to complete the reaction cycle. In a strong acid solution the homogenous reaction is extremely slow [15–18, 21], and yet our results indicate significant quantities of sulfur dioxide can be converted in the cell, apparently by chemical reaction with ferric ion. Residence time of the anolyte in the electrochemical reactor is only several minutes even at the slowest flow (4.6 min at 0.3 ml min^{-1}).

Since heterogeneous reaction, catalysed by the graphite, can account for the enhanced rate, some graphite catalysed ferric-sulfur dioxide reactions were studied in glass batch reactors by combining mixtures of 0.04 M Fe^{3+} and 0.11 M SO_2 with graphite and 0.049 M ferrous ion in 3 M sulfuric acid. The extent of reaction was monitored through the ferric ion concentration. Concentration–time plots are shown in Fig. 8 for three experiments, and indicate a strong heterogeneous catalysis. In the presence of graphite the ferric ion reacted rapidly compared with the homogenous reaction, representing an increase in the early reaction rate of over three orders of magnitude. An important feature of the catalyzed reaction is the significant rate drop as the reaction progresses. Empirically, it was found that the iron concentration decreased roughly linearly with the log of time. This effect may be associated with inhibition arising from the ferrous ion product. This was supported by the effect of adding 0.049 M ferrous ion to the above ferric–sulfur dioxide mixture in the presence of graphite (Fig. 8). The rate of decrease in the ferric concentration of the mixture is slower and the early rapid rate seen with the ferric solution is not observed. The heterogeneous reaction is inhibited by the iron(II) concentration, but is nonetheless fast compared to the solution reaction. Other experiments with activated carbons showed a similar catalytic enhancement, indicating a general effect. Since carbons often have a larger surface area than graphites, they can potentially be far more reactive on a per gram basis.

Catalysis of solution reactions by solids have been described and reviewed, in large part recently by Spiro and coworkers [32–34]. Carbons also have been reported to catalyse a number of oxidation–reduction reactions, including the reaction between ferricyanide and sulfite [34, 35]. Not all solution reactions cata-

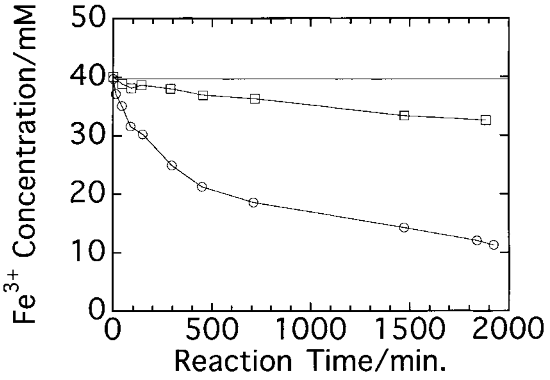

Fig. 8. Kinetic reaction plots of the iron(III) concentration versus time plots for the graphite catalysed reaction of solution, all initially containing 0.040 M Fe^{3+} and 0.11 M SO_2 (fixed concentration) in 3 M sulfuric acid at room temperature (near 24 °C). (○) 2.2 g graphite; (□) 2.2 g graphite and 0.049 M Fe^{2+}; (solid line) no graphite.

lysed by solids involve the transfer of electrons, but in those that do, the solid catalyst is often an electrical conductor and an electrocatalyst (i.e., a noble metal). In such a case, electron flow may occur through the bulk of the solid with two electrochemical half-reactions, occurring on separate surface sites in a local cell. The redox process can be divided over large areas and requires interaction of the reactants with the surface. With regard to the present work, this mechanism does not seem probable. The graphite catalysed electrochemical reaction of adsorbed sulfur dioxide is slow even at potentials significantly higher (see Fig. 7) than the iron redox reaction potential ($E^{\circ\prime} = 0.68\,\mathrm{V}$ for 1 M sulfuric acid [9]). Additionally, all aspects of the electrochemical work indicated that iron was the dominant adsorbed species under the conditions studied. Access of sulfur dioxide to the graphite surface would be limited, and the rate correspondingly reduced. An alternative mechanism using surface bound ferric ions interacting with a solution sulfur dioxide molecule, appears more likely. The strongly inhibiting effect of the ferrous ion may result from competitive adsorption of surface sites. For SO_2 to be oxidized to sulfuric acid two one-electron transfers to the ferric ion are required, perhaps from two different absorbed ferric ions. Ferrous ion may block electron transfer possibilities.

Studies on the reaction of sulfur dioxide have mostly used either carbon or iron as the catalyst; combinations of the two are rarely used [36]. This may be of some significance in the atmospheric catalysis of SO_2 oxidation, where iron(III) ions and carbon particles (soot) have been shown individually to be active [37, 38].

Graphites (or carbon) are effective catalysts for the iron mediated sulfur dioxide reaction in strong acid solutions and might be further used to remove sulfur dioxide from the electrogenerative reactor effluent. In flow reactors the build-up of ferrous ion would be less detrimental. The approach here and variants on these systems provide opportunity for enhancing an otherwise slow reaction and should find application for sulfur dioxide conversion schemes.

3.4. *Outlook and interpretation*

A goal of this work was to explore possibilities for a regenerable sulfur dioxide conversion process, which might operate at higher acid concentrations to promote sulfuric acid recovery without expensive catalysis. The graphite catalysed electrogenerative reactor operating with iron mediation appears promising and might be employed in several schemes. No attempt was made to optimize the performance of either the electrogenerative reactor or the following graphite catalytic stage. A preferred mode of operation for the electrogenerative reactor would involve use of higher iron concentrations with large ferric to ferrous ion ratios. A high ferric content of the effluent would facilitate operation of a following graphite catalytic reactor.

In the electrogenerative reactor the graphite serves a dual role as an electrode for reoxidizing the iron and as a catalyst for the ferric-sulfur dioxide reaction. The combined properties of the graphite give a flow-type electrochemical reactor a distinct advantage over catalytic reactors, in terms of reducing the surface concentration of the ferrous ion product, which inhibits the graphite catalyzed reaction. In an operating electrochemical reactor the surface concentration of ferrous ion is kept low by electrochemical reaction, but it will accumulate in a chemical reactor and is only removed from the graphite surface by transport. Even so, both types of reactors might be utilized in tandem with graphite catalysis of the Fe(III)–SO_2 reaction operating in a second reactor.

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